

Growing Diamond Crystals by Chemical Vapor Deposition



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The synthesis of large single-crystal diamonds by chemical vapor deposition (CVD) at high growth rate has opened a new era for applications of the material. Large and thick single crystals can now be produced at very high growth rates, and the mechanical properties, chemistry, and optical and electronic properties of the material can be tuned over a wide range. The single crystals can have extremely high fracture toughness and exceptionally high hardness following high-pressure/high-temperature annealing. CVD single-crystal diamonds will make possible a new generation of high-pressure-temperature experimentation to study Earth and planetary materials and should enable a variety of other new scientific and technological applications.

KEYWORDS: Diamond, chemical vapor deposition, carbon, high pressure, diamond anvil cell

INTRODUCTION

By every measure, diamond is a unique material. The supreme hardness, singular strength, high thermal conductivity, low thermal expansion, chemical inertness, excellent optical, infrared, and X-ray transparency, and semiconductor properties of the material continue to attract scientific and technological interest worldwide. However, the lack of large, high-quality single crystals of diamond prevents its use in many applications. Although the impurity content, strain, and overall quality of diamonds produced by high-pressure/high-temperature techniques (HPHT; e.g., >4.5 GPa, ~1200°C) have improved in recent years (Barnard 2000; Hazen 1993), these diamonds cannot be produced as perfect single crystals in the range of several tens of carats. Instead, they are limited commercially to up to ~3 carats (or 0.6 g, roughly 7 mm across). In addition, diamond crystals need to be produced in different shapes for many applications (e.g., as large plates). Indeed, our imagination regarding the applications of single-crystal diamond in many ways has been circumscribed by the limited size of available high-quality HPHT diamond crystals, created either by nature or in the laboratory.

One of the most important developments in diamond synthesis is Chemical Vapor Deposition (CVD). The first attempt at creating diamond using this process was reported by Eversole in 1949 (see Liu and Dandy 1995). This discovery launched a significant period of exploration of various CVD techniques for synthesizing diamond films and coatings in the 1980s (Kamo et al. 1983; Spitsyn et al. 1981). In 1982, a group at the National Institute for Research in

Inorganic Materials (NIRIM) reported growth rates for diamond films of up to $10 \mu\text{m h}^{-1}$ (Matsumoto et al. 1982). The production of single-crystal particles, polycrystalline films, and epitaxially grown films using the CVD method started in the late 1980s (Kamo 1990). Most of the thick (greater than $10 \mu\text{m}$) polycrystalline diamond films produced then were not transparent. In 1992, General Electric (GE) demonstrated the technology for producing thick and transparent polycrystalline CVD diamond films (Anthony and Fleischer 1992). During this period, CVD diamond was grown at low growth rates up to a few $\mu\text{m h}^{-1}$ at substrate

temperatures below 1000°C in hydrogen gas mixtures with a low concentration of methane (typically 0.1–2%).

Under the auspices of the NSF Center for High Pressure Research, our group at the Carnegie Institution launched a program with the University of Alabama–Birmingham (UAB) in the mid-1990s to produce large homoepitaxial single-crystal diamonds. This work resulted in the development of the high-temperature (>1000°C) and relatively high-pressure (150 torr) processes that led to the growth of single-crystal diamond at very high growth rates (Yan 1999). During the current decade, developments in this technique have overcome some of the constraints of HPHT methods. The technique can be used to coat diamonds on various materials, control the doping with other elements, and grow diamonds of larger sizes. Single-crystal diamonds can now be produced at very high growth rates of 50–150 $\mu\text{m h}^{-1}$ (Yan et al. 2002), and the fabrication of these crystals can be tuned to exhibit remarkable mechanical properties (Yan et al. 2004).

CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition (CVD) involves a series of gas-phase and surface chemical reactions and the deposition of reaction products, i.e., diamond, on a solid substrate surface. For diamond deposition, a carbon-containing precursor is required for diamond nucleation and growth. Many gas-phase carbon sources can be used, and methane is the most common. In 1981, it was found that adding atomic hydrogen to the CVD process stabilized the thermodynamically metastable diamond surfaces and promoted diamond growth, preferentially etching non-diamond carbon deposits and giving growth rates of the order of one $\mu\text{m h}^{-1}$ (Spitsyn et al. 1981). Unlike HPHT synthesis, which is typically carried out at pressures in excess of 5 GPa, diamond

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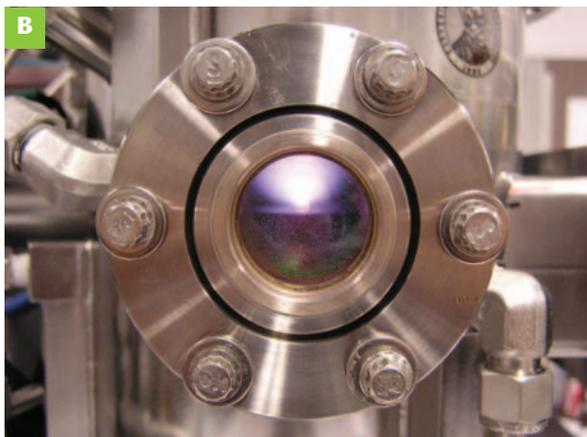
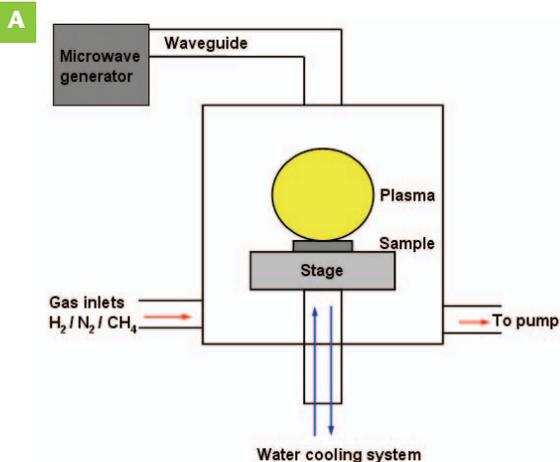


FIGURE 1 **A.** Schematic diagram of a microwave plasma CVD chamber; **B.** Photograph of a diamond growing in the CVD chamber (Model: SEKI AX5400). The substrates can be Si, Mo, or other materials for heteroepitaxial growth, as well as natural or synthetic diamond plates for homoepitaxy.

CVD is usually done at a fraction of one atmosphere. The deposition is controlled by strongly coupled parameters, all of which have an impact on the final product. In general, the substrate temperature, the concentration of plasma species, and the substrate materials determine the crystallinity of the growing material.

CVD techniques are generally applied using various methods to activate the gases to generate radicals responsible for the deposition. Electrical discharge CVD, especially microwave plasma CVD, is now the most widely used technique for diamond deposition (Fig. 1). Microwaves dissociate the molecules in the gas to generate a plasma containing carbon atoms for deposition onto the substrate surface. The substrate is heated by the absorption of microwaves, the bombardment by energetic plasma species, and exothermic recombination of radicals such as atomic hydrogen on the diamond growing surface.

SINGLE-CRYSTAL CVD DIAMOND

Single-crystal, homoepitaxial growth of diamond is being carried out by a growing number of research groups (Martineau et al. 2004). Homoepitaxial growth of single-crystal diamonds uses diamond as the substrate material. Several research groups have produced thin homoepitaxial layers, usually less than 0.1 mm thick. In the 1990s, fabrication of thicker layers was reported (Badzian and Badzian 1993; Janssen et al. 1990; Linares and Doering 1999; Plano



FIGURE 2 Modified, brilliant-cut, single-crystal diamond grown by CVD. The crystal is 2.45 mm high and was grown in one day. The top 0.5 mm (table) of the crystal is a yellow Type Ib HPHT substrate; thus the yellow tint is due to internal reflection (the CVD diamond is transparent and colorless) (Yan et al. 2004).

et al. 1994; Schermer et al. 1994). Most recently, the Carnegie group reported high-quality single crystals with thicknesses of 4.5 mm (Yan et al. 2004).

For bulk single-crystal diamond deposition, single-crystal diamond substrates are used, since the quality of the substrates is strongly affected by the quality of the substrates. Single-crystal CVD diamond deposition on single-crystal HPHT synthetic substrates was accomplished in the early 1990s by plasma torch CVD (Snail et al. 1991) at growth rates of 100–200 $\mu\text{m h}^{-1}$, but there are significant difficulties with precise temperature and growth control with this technique. Growth by hot filament (Vitton et al. 1993) and microwave plasma (Tzeng et al. 1993; Vitton et al. 1993) yields stable growth conditions, but for years the growth rates were low (0.1–10 $\mu\text{m h}^{-1}$), and most plates produced were only 0.1–1 mm thick. Single-crystal CVD diamonds have been used by Element Six and Sumitomo in electronics applications (Isberg et al. 2002; Okushi 2001) and by Apollo Diamond as gems (Wang et al. 2003). Boron, whose presence in diamond transforms it from an electrical insulator into a *p*-type semiconductor, can be introduced during the growth process, and development of boron-doped CVD diamond for electronic applications is in progress (Kondo et al. 2002). Large-scale industrial production of single-crystal CVD diamonds has not yet occurred because of the high costs when the growth process is slow (such as 0.1–10 $\mu\text{m h}^{-1}$), the limited size of the substrates (maximum area around 10 × 10 mm), and the poisoning of surfaces by twins and polycrystalline structures (Angus et al. 1992; Tamor and Everson 1994). Many of these problems and limitations have recently been overcome.

Working originally with the UAB team, the Carnegie Institution group has focused on the growth of large, single-crystal CVD diamond for use as anvils in high-pressure research. Producing large and durable diamonds at high growth rates with high strength, absence of twinning, and optical transparency are the main goals and challenges. This work led to optimal conditions for enhancing growth rates and producing smooth, twin-free {100} diamond surfaces (Yan 1999). With high gas pressures of 150 torr, methane concentrations up to 20% in the CH_4/H_2 gas mixture, and the addition of a small amount of nitrogen gas, diamond growth rates of up to 150 $\mu\text{m h}^{-1}$ were achieved (Yan et al. 2002), much faster than the typical CVD diamond growth rate of 1 $\mu\text{m h}^{-1}$. The growth-rate enhancement with the addition of nitrogen is consistent with



FIGURE 3 **A.** Photograph of a typical, three-dimensional, as-grown CVD crystal sitting atop a type 1b substrate. The CVD layer is 1.2 mm thick and was grown in 12 hours. The yellow color is due to the substrate. **B.** Left: 5 × 5 × 0.5 mm diamond plate grown in about 5 hours by CVD. Right: plate produced by De Beers. **C.** Color changes after HPHT annealing: (i) brown, as-grown CVD layer deposited on yellow type 1b HPHT seed; (ii) annealed at 1900°C and 6.5 GPa for 1 hour—CVD layer turned blue; (iii) annealed at 2200°C and 7.0 GPa for 10 hours—CVD layer turned colorless while the substrate became light yellow (from Charles et al. 2004).

observations for polycrystalline diamond films (Muller-Sebert et al. 1996). This microwave plasma CVD method can routinely produce one 3 mm-thick, twin-free, gem-quality diamond in approximately one day (FIG. 2). Interestingly, single crystals produced in this way exhibit very high toughness (Yan et al. 2004).

In addition to controlling the variety of impurities that can be introduced for electronic applications, challenges for single-crystal CVD diamond growth include producing large-area plates (>10 × 10 mm) and large-volume crystals (>10 × 10 × 10 mm, >20 carats), as well as improving crystal quality (i.e., reducing strain). Microwave plasma CVD permits growth on a single surface of the diamond substrate. Potential solutions for producing larger area CVD diamonds include use of a mosaic or tile arrangement of several {100}-surfaced diamond seeds (Kobashi et al. 2003), 3-dimensional growth on multiple {100} faces, and enlargement of each surface (FIG. 3A).

Diamond produced by the high-growth process is classified as Type IIa (nitrogen <20 ppm) and can be made transparent (FIG 3B). On the other hand, yellow material grown under certain conditions can be subjected to high P-T annealing to produce transparent material. In fact, brown

single-crystal CVD diamond annealed at 2000°C and 5–7 GPa results in color changes (FIG. 3c) (Charles et al. 2004; Yan et al. 2004) (see also Shigley, this issue). In addition, the hardness of the material can be significantly enhanced, beyond that of conventional natural and as-grown synthetic diamonds (Yan et al. 2004). The high fracture toughness of the material prior to annealing and the enhancement of the hardness correlate with changes in the mosaic character of the crystals and transformation of residual carbon defects present in the as-grown crystals.

APPLICATIONS OF LARGE SINGLE-CRYSTAL CVD DIAMOND

A principal goal of the Carnegie effort has been to produce large, single-crystal diamonds for new classes of high-pressure devices (FIG. 4). These would be used to pressurize significantly larger samples at very high pressures and reach much higher pressures and temperatures in the laboratory (e.g., 500 GPa, or 5 megabars). For this, we need very large (e.g., many tens of carats), ultrastrong, single-crystal diamond material that is simply not available in nature and cannot be produced by current HPHT methods (Hemley and Mao 2002). Such diamonds will allow a broad range of

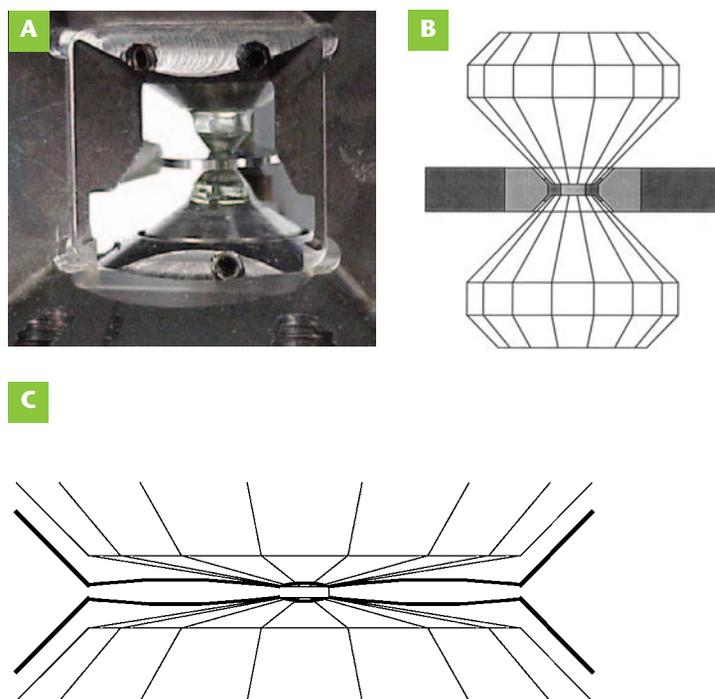


FIGURE 4 **A.** Example of a current 'panoramic' cell, shown here with 'conventional' 0.3 carat diamonds. This type of device can be scaled up in size for anvils in the tens of carat range (centimeter dimensions) and is also currently used with other high-strength gems such as moissanite (single crystal SiC) (Xu et al. 2004). In addition to using large diamond crystals with significantly larger culets, a 'belt' can be placed around the anvils (**B**) to provide additional support at higher loads and to increase sample thickness. The anvil tips can be shaped by micromachining techniques to further enhance sample volume. An example is shown in (**C**), which is the shape to which diamonds deform at very high loads (Hemley et al. 1997); it is also the pre-formed shape of 'toroidal anvils' used in lower pressure devices (see Hemley 1998). The sample volume is enhanced without sacrificing the versatility of conventional diamond anvil cells. This will make possible new kinds of experiments at very high pressures, such as NMR, inelastic neutron scattering, and in situ petrology studies.

experiments that cannot yet be performed under the P-T conditions that prevail not only within our planet but also within the larger planets in this and other solar systems. Already, the first experiments have been conducted at close to 200 GPa with CVD-grown diamond anvils (Mao et al. 2003).

There are many other applications of large, single-crystal CVD diamonds that derive from the unique hardness, toughness, electrical properties, and thermal conductivity of diamond. The excellent hardness and toughness of the single-crystal CVD diamond grown at high growth rate is potentially important for high-precision cutting tools. With diamond's uniquely high thermal conductivity and low coefficient of thermal expansion, fabrication of monolithic heat spreaders or microchannel structures from single-crystal CVD diamond would perform well beyond that of thin diamond films in high-power thermal management applications. The availability of large, transparent single-

crystal diamonds will greatly extend their use as far-infrared or high-power microwave windows. In each of these applications, chemical and thermal shock resistance is an important feature. Other applications include large electron field emission sources, micro-electromechanical systems, surface acoustic wave devices, and large semiconductor devices. In conclusion, with the rapid progress in the development of CVD diamond, and especially with advances in single-crystal diamond growth during the last 2–3 years, the full potential of diamond for a broad range of applications is being realized.

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